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SOME LOW-COST COUNTER ELECTRODE MATERIALS FOR CdS AND CdSe QDSSCs*

6.1 Introduction

In order to obtain a high performing QDSSC, materials selection plays a major role [1]. The type of QD sensitizers, counter electrode (CE) materials and electrolyte composition could affect the overall performance in one way or another. Among the prominent materials for QD sensitizers, CdS and CdSe are widely used due to their ease of preparation. The QDSSCs based on them usually employ polysulfide based liquid electrolytes. For CE, the usual choice is platinum even though other materials such as gold, Cu₂S and reduced graphene oxide (RGO) are possible [2-4].

In this work, alternative low-cost CE materials were used in CdS and CdSe QDSSC assembly to understand the effect of CE materials towards the solar cell

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performance. The materials for the CEs used were commercially obtained or prepared economically at lab scale. Two different optimized polysulfide liquid electrolytes were used in the CdS and CdSe QDSSCs. Photoelectrochemical performance of the cells was investigated to assess the effect of the CE materials. The behaviour of the QDSSCs were also investigated using electrochemical impedance spectroscopy (EIS).

CdS and CdSe QD-sensitized TiO₂ electrodes were prepared as described in Chapter 3. SILAR parameters for CdS and CdSe QD were set in accordance with the optimization result as reported in Chapter 4. Polysulfide electrolyte for CdS QDSSC was prepared according to procedure outlined in Chapter 4 while for CdSe QDSSC, it was prepared based on the outcome of the study in Chapter 5. Five types CE materials were used: commercial platinum solution (Plastisol, Solaronix), graphite, carbon, Cu₂S and RGO. The preparation of the CEs were as per procedure in section 3.3, Chapter 3. Solar cells performances and their respective EIS results were acquired as per procedure in section 3.4, Chapter 3.

6.2 Results and discussion

CdS and CdSe QDSSCs have been fabricated with QD-sensitized TiO₂ layers prepared via SILAR method and selected liquid electrolytes. Both CdS and CdSe QD-sensitized TiO₂ layers were assembled with five different types of CE materials including platinum. The cell with platinum as the CE was used as the reference cell. The *J-V* curves for both types of QDSSCs showed that solar cell performance is considerably influenced by the choice of CE materials.

For CdS QDSSCs, the J - V curves are shown in Figure 6.1 while Table 6.1 summarizes the performance properties. Higher efficiencies of 1.06%, 1.20% and 1.16% are observed for solar cells assembled with commercial platinum catalyst, graphite layer and carbon soot respectively as CE materials. The solar cells with these CE materials produce a current density above 6.00 mA/cm^2 . This result indicates that carbon based material (graphite and carbon soot) can be the alternative CE for CdS QDSSCs. On the other hand, Cu_2S and RGO do not give better performances in this CdS QDSSC although better performances with these materials have been reported by other researchers with efficiencies above 3% [5,6]. The low performance of QDSSCs with Cu_2S and RGO as CEs is attributed to overall low short-circuit current density, open-circuit voltage and fill factor. Nevertheless, the observed photocurrent density for the cell with Cu_2S as CE is comparable with the published result of 3.06 mA/cm^2 [7]. In general, CdS QDSSCs exhibit low fill factors (less than 40%) with any of the tested CE materials.

In the study of CdSe QDSSCs, J - V curves of each solar cell combination with different CE materials are shown in Figure 6.2 and the corresponding performance data are summarized in Table 6.2. Unlike the CdS QDSSC, CdSe QDSSC exhibits high efficiency with Cu_2S and platinum as CE materials. Among these results, the best performance is observed in solar cell assembly with commercial platinum catalyst as CE. It recorded an efficiency of 1.41% followed by 1.16% in the QDSSC having Cu_2S as the CE. The fill factor and V_{oc} with Cu_2S are also good. These results show that Cu_2S is compatible with CdSe as a CE material. On the other hand, carbon based materials like graphite layer and carbon soot which work well in CdS QDSSC, perform poorly when coupled with CdSe QD-sensitized TiO_2 electrode. The poor performance from these materials could be attributed to the low electrocatalytic activity at

CE/electrolyte interface against the fast electron injection and transfer from CdSe QDs into the photoanode substrate. The preference of different CE materials towards CdS and CdSe QD-sensitized TiO₂ electrode could be explained by EIS study.

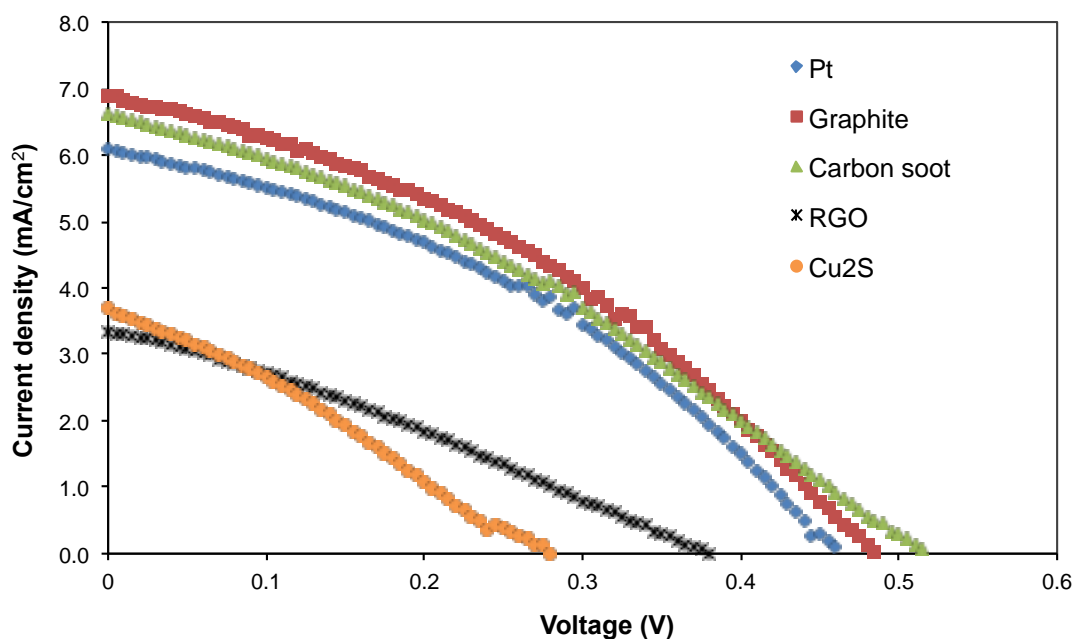


Figure 6.1 J - V curves of CdS QDSSCs with various CEs.

Table 6.1: Performance parameters of CdS QDSSCs with various CEs

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
Pt	6.09	0.460	38	1.06
Graphite	6.89	0.485	36	1.20
Carbon soot	6.62	0.515	34	1.16
Cu ₂ S	3.70	0.280	28	0.29
RGO	3.35	0.380	29	0.37

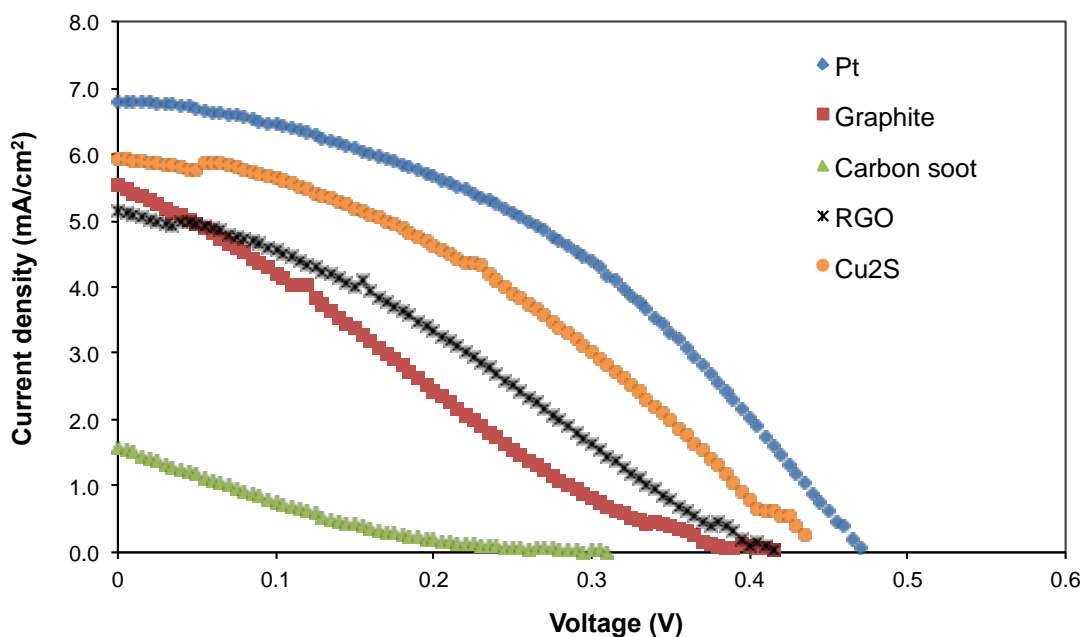
Figure 6.2: J - V curves of CdSe QDSSCs with various CEs

Table 6.2: CdSe QDSSC performance parameters with various CEs

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
Pt	6.80	0.470	44	1.41
Graphite	5.53	0.415	22	0.50
Carbon soot	1.58	0.310	15	0.07
Cu ₂ S	6.01	0.430	45	1.16
RGO	5.15	0.415	31	0.66

EIS is performed to understand the kinetic processes within the QDSSC. Typically, an EIS spectrum for a dye-sensitized solar cell (DSSC) consists of three semicircles in the Nyquist plot [8]. This characteristic is also applicable to QDSSC [7]. The three semicircles correspond to the response at high-frequency, intermediate-frequency and low-frequency regions when the cell is biased at its open circuit potential. Response in the high-frequency region is attributed to the charge transfer between electrolyte and CE interface while intermediate-frequency response denotes the electron transport in the QD-sensitized TiO₂ layer and the recombination process at the QD-sensitized TiO₂ and electrolyte interface. Finally, the low-frequency response reveals the diffusion process in the electrolyte. Generally, a double arc is observed for low

performance QDSSC where the feature of electrolyte diffusion is seldom present. In this study, the focus is on the first semicircle which is the response at high-frequency. Typically, the equivalent circuit of QDSSC in a conductive state is a combination of a series resistance and two time constant elements as shown in the insets of Figure 6.3(a) and 6.4(a) [9]. The first time constant element represents the response at CE/electrolyte interface. The time constant element in the circuit represents a resistor in parallel with a constant phase element (CPE).

CdS QDSSCs were studied with EIS at 0.45 V potential bias. The potential bias is selected at the approximate median of the observed open circuit voltage results. Meanwhile, for CdSe QDSSCs, the measurements were carried out at a bias of 0.40 V. Figure 6.3(a) shows the Nyquist plot of CdS QDSSCs having various CE materials under dark condition and the details of the high-frequency response are shown in Figure 6.3(b). The result in dark condition serves as a reference for the result under illumination (Figure 6.3(c) and (d)). The corresponding series resistance and charge-transfer resistance data obtained are tabulated in Table 6.3.

From the EIS result it can be seen that the CdS QDSSC with Cu_2S as CE has the lowest series resistance (R_s). This is reasonable considering the highly conductive brass metal involved in comparison to the usual FTO layer used. R_s is the resistance corresponding to the transport resistance of the conducting substrate. In this study, charge transfer resistance at the QD-sensitized TiO_2 /electrolyte interface (R_r) is not discussed as the value is not directly influenced by the choice of counter electrode materials. Under dark condition, the charge-transfer resistance at the CE/electrolyte interface (R_{CE}) is high in all the cells. When the cells were tested under illumination, the R_{CE} reduced substantially for most of the cells due to more charge transfer in the system.

It is observed that the low R_{CE} gives rise to higher open circuit voltage of the cell as seen in the case of QDSSCs with carbon soot and platinum as their CEs. However, this is not the case for Cu_2S as its photocurrent density is few times lower than that of the cell with platinum as CE. The low R_{CE} could be due to the excessive potential bias applied to the cell as its open-circuit voltage is only 0.28 V. This high potential bias could have provided a more conductive state for the charge transfer. The overall low performance of the cell could be attributed to the low catalytic activity at Cu_2S /electrolyte interface which implies a slow reduction rate for polysulfide S_x^{2-} species. For the high efficiency CdS QDSSCs having platinum, graphite or carbon soot as CE, the good performance is due to low CPE values. This translates to low true capacitance at CE/electrolyte interface which could imply an active electrocatalytic activity.

EIS results for CdSe QDSSCs are shown in Figure 6.4 with the corresponding reference data under dark condition depicted in Figure 6.4(a) and (b). The related series and charge-transfer resistances are tabulated in Table 6.4. Like in the CdS QDSSC, low R_S is observed in the cell with Cu_2S as CE. In high performing cells where platinum and Cu_2S are the CEs, the observed low R_{CE} coupled with low CPE value lead to high catalytic activity at the CE/electrolyte interface. On the other hand, cells with CE from carbon based materials show high CPE value which results in slower charge transfer through the interface. However, as an exception, R_{CE} for cell with carbon soot as CE appears to be low due to the lower open circuit voltage compared to the applied potential bias. The R_{CE} could be even higher should the applied potential bias equals the open-circuit voltage. Contrary to general observation, the cell with RGO as the CE has lower R_{CE} under dark condition than the value obtained under illuminated condition. It is to be suspected this could be due to inhomogeneous dispersion of the RGO flakes on

the substrate. As a result, there might be less electrochemical active area for the reduction of polysulfide species S_x^{2-} .

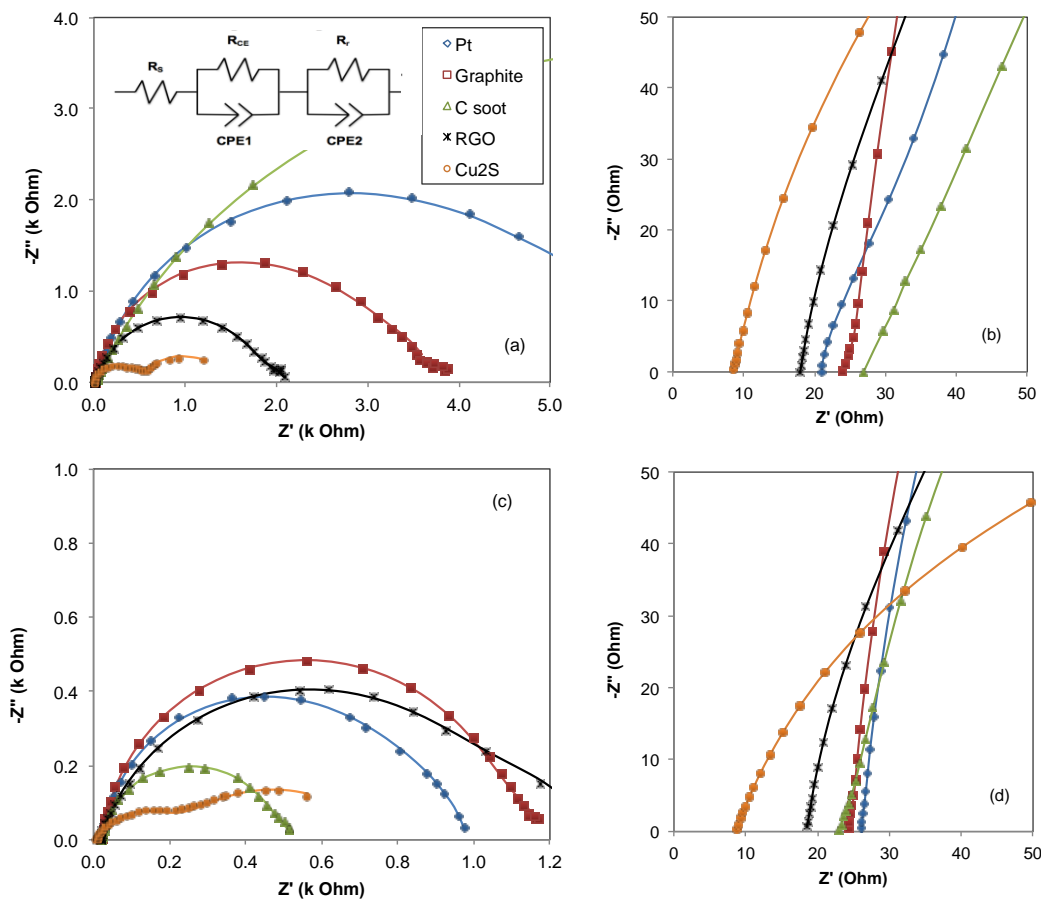


Figure 6.3: (a) Nyquist plots of CdS QDSSCs under dark; the equivalent circuit of the QDSSC with the representation of impedance at CE/electrolyte interface (subscript CE), QD-sensitized TiO_2 /electrolyte (subscript r) and series resistance (subscript s). The symbol R and CPE denote the resistance and constant phase element, respectively. (b) Details of plots (a) at high frequency. (c) Nyquist plots of the same cells under 1000 W/m^2 illumination. (d) Details of plots (c) at high frequency. The solid lines are the fitted curves.

Table 6.3: EIS results of CdS QDSSCs with different CEs under 1000 W/m^2 illumination and dark (showed in parenthesis): series resistance, charge-transfer resistance and impedance values of the CPE.

	R_s (Ω)	R_{CE} ($k\Omega$)	CPE1-T ($\mu S.s^n$)	CPE1-P ($0 < n < 1$)
Pt	26.12 (20.45)	0.71 (3.19)	3.03 (55.78)	0.96 (0.68)
Graphite	24.32 (24.31)	1.03 (1.08)	3.55 (128.10)	0.94 (0.81)
Carbon soot	23.10 (26.84)	0.40 (7.21)	4.92 (31.13)	0.94 (0.73)
Cu_2S	7.88 (8.15)	0.20 (0.46)	52.64 (18.41)	0.71 (0.84)
RGO	17.62 (17.45)	1.02 (1.83)	10.46 (11.13)	0.82 (0.83)

Since polysulfide electrolyte could impair the platinum CE surface as reported by Mora-Sero *et al.*, the performance of such cell could be reduced over the long run [10]. Ultimately, the charge-transfer resistance will increase. As such, Cu_2S appears to be a good candidate for CE material for CdSe QDSSCs. Nevertheless, the high performance as observed in both CdS and CdSe QDSSCs with platinum CE suggests the detrimental effect from polysulfide electrolyte might not be that serious at the early stage of operation. Based on the EIS observation, should a multilayered CdS/CdSe QDSSC be prepared, a composite between carbon and Cu_2S could be the best materials for the CE. Similar conclusion has been made by Deng *et al* [9]. It is to be noted that the different EIS parameter values obtained for both CdS and CdSe QDSSCs with similar CE materials can be partly attributed to the different choice of electrolytes used as well.

The efficiencies reported in this study are somewhat lower than the values reported in the literature for similar QDSSCs. It should be noted that the present study was undertaken with standard TiO_2 layer sensitized with a single QD layer and standard electrolytes to explore the best CE materials, which resulted in lower efficiencies. The efficiencies can be improved considerably with optimization of all the components involved in the QDSSC and by using passivation layers to reduce the charge recombination losses.

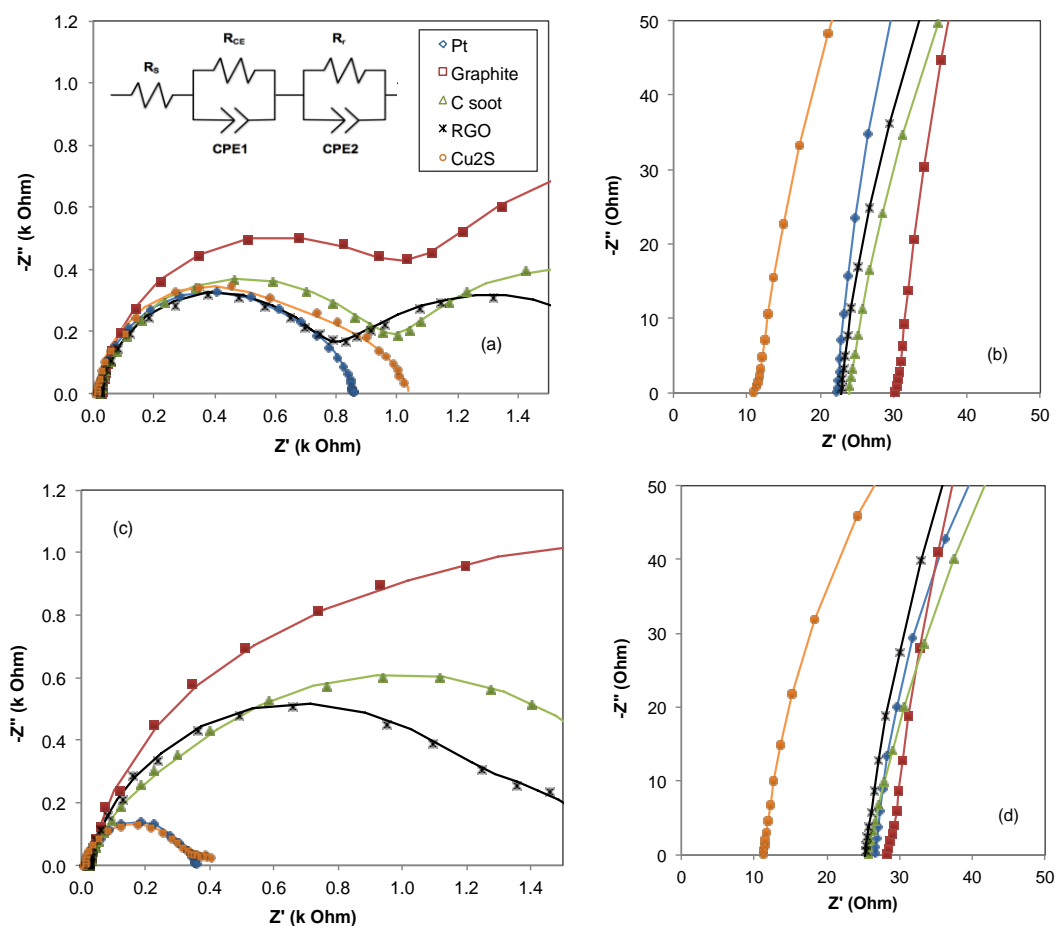


Figure 6.4: (a) Nyquist plots of CdSe QDSSCs under dark; the equivalent circuit of the QDSSC with the representation of impedance at CE/electrolyte interface (subscript CE), QD-sensitized TiO_2 /electrolyte (subscript r) and series resistance (subscript s). The symbol R and CPE denote the resistance and constant phase element, respectively. (b) Details of plots (a) at high frequency. (c) Nyquist plots of the same cells under 1000 W/m^2 illumination. (d) Details of plots (c) at high frequency. The solid lines are the fitted curves.

Table 6.4: EIS results of CdSe QDSSCs with different CEs under 1000 W/m^2 illumination and dark (showed in parenthesis): series resistance, charge-transfer resistance and impedance.

	R_s (Ω)	R_{CE} ($\text{k}\Omega$)	CPE1-T ($\mu\text{S}\cdot\text{s}^n$)	CPE1-P ($0 < n < 1$)
Pt	26.84 (22.29)	0.28 (0.58)	3.11 (4.57)	0.97 (0.96)
Graphite	28.06 (30.30)	0.88 (0.97)	13.52 (6.15)	0.91 (0.94)
Carbon soot	25.01 (23.22)	0.11 (0.93)	15.17 (10.08)	1.00 (0.86)
Cu_2S	11.25 (11.28)	0.28 (0.53)	8.09 (3.98)	0.94 (1.00)
RGO	24.48 (22.80)	1.19 (0.71)	8.89 (4.86)	0.86 (0.90)

6.3 Summary

Low-cost CEs have been prepared from graphite, carbon soot, Cu_2S and RGO to study their effect on the performance of CdS and CdSe QDSSCs. Carbon-based materials were found to be a good CE material for CdS QDSSCs where the cell performance reached the best efficiency value of 1.20% with the highest photocurrent density. For CdSe QDSSCs, although platinum showed a relatively good performance, Cu_2S could be the alternative choice for CE. EIS measurements on both CdS and CdSe QDSSCs showed that low R_{CE} and CPE values for the CE/electrolyte interface are the key criteria for selecting good performance CE materials. Further optimization of the cell is possible for achieving higher efficiencies.

6.4 References

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